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Observation of a Spin-Peierls Transition in a Heisenberg Antiferromagnetic Linear-Chain System*

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Magnetic-susceptibility and EPR measurements are reported which provide the first unambiguous evidence for a spin-Peierls transition in a system of linear one-dimensional antiferromagnetic Heisenberg chains. The material studied is $TTFCuS_4C_4(CF_3)_4$ (TFF stands for tetrathiafulvalinium). At 12 K, the spin-lattice system undergoes a second-order phase transition to a singlet ground state.

There has been much interest recently in the unusual electrical conducting properties of quasi-one-dimensional systems such as tetrathiafulvalene tetracyanoquinodimethane. Several of these materials seem to undergo a Peierls transition[1] to an insulating ground state.[2] The magnetic analog, the spin-Peierls transition, has been discussed theoretically[3,4] for antiferromagnetic (AF) chains. At this transition the spin-lattice system dimerizes and the material undergoes a second-order transition to a singlet ground state with a magnetic gap. We report the first unambiguous evidence, from magnetic measurements, for such a transition.

The material studied is tetrathiafulvalinium bis-*cis*-(1, 2-perfluoromethylethylene-1, 2-dithiolato)-copper [or, $TTFCuS_4C_4(CF_3)_4$]. It is a member of a series of $TTFMS_4C_4(CF_3)_4$ (M=Cu, Au, Pt, or Ni) donor-acceptor compounds, whose preparation and characterization are reported elsewhere.[5] These materials are obtained as needlelike crystals, 2–3 mm long and ~0.05 $\times$0.3 mm^2 in cross section, by slow cooling of acetonitrile solutions. Their formulation as ionic materials rests on the results of solution-conductivity measurements, spectral studies, EPR, and magnetic-susceptibility measurements.[5] The TTF cation should have one unpaired electron located in a singly degenerate π orbital of b_{1u} symmetry[6] (D_{2h}). On the other hand, the $MS_4C_4(CF_3)_4$ anion (M =Cu or Au) is diamagnetic with two electrons in the highest occupied b_{2g} (D_{2h}) π orbital.[7]

A complete structure determination for $TTFCuS_4C_4(CF_3)_4$ has not been done, but a study of single crystals with the x-ray precession technique shows that the Cu compound is isostructural with the corresponding Pt derivative for which a full structure determination[3] has been made. Their space groups are the same and their lattice parameters and diffraction intensities of corresponding reflections are quite similar. The true space group is $P\bar{1}$, with one formula unit per unit cell, but it is convenient to describe the structure in terms of a face-centered cell with $Z=4$ and space group $F\bar{1}$. With that description for the Cu compound, $a=23.1$ Å, $b=13.2$ Å, $c=7.80$ Å, $\alpha=92.7°$, $\beta=101.8°$, and $\gamma=90°$.

The molecular arrangement is shown in Fig. 1. There occurs an alternate stacking of the two kinds of ions along c axis, as well as alternation along the a and b axes. The molecular planes of both kinds of ions are nearly parallel to the (001) planes, and the protrusion of π orbitals from these planes strongly favors electronic interaction along the c axis. The alternate stacking arrangement of oppositely charged ions and their

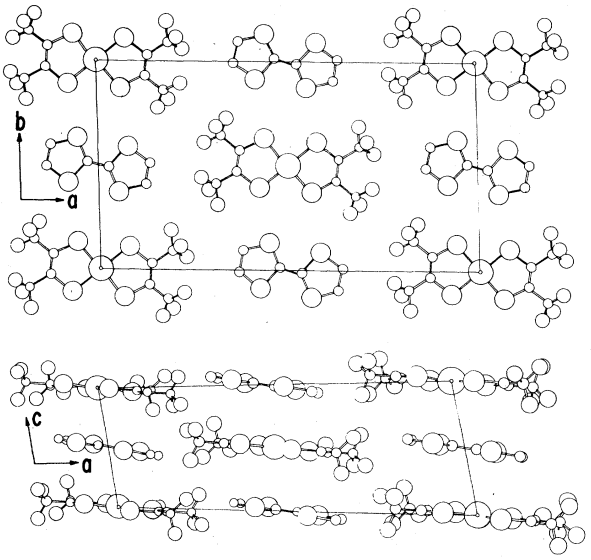

FIG. 1. View of $TTFCuS_4C_4(CF_3)_4$ structure in the a-b and a-c planes. The $CuS_4C_4(CF_3)$ anion is at the corners and face centers. The TTF cation is at the midpoint of each edge.

large separation (~3.9 Å) implies highly localized electron orbitals, a fact borne out by the conductivity which is less than 10^{-9} $(\Omega\ \mathrm{cm})^{-1}$ by four-probe dc measurements on a single crystal. Thus, from the structure we anticipate linear magnetic chains along the c axis with probable AF interaction of the spins on the TTF cation via superexchange through the $CuS_4C_4(CF_3)_4$ anion.

The static susceptibility was measured between 2.5 and 300 K with the Faraday method using an electrobalance and a split superconducting solenoid. The samples consisted of several tens of single crystals (total mass 2.18 mg), which were aligned with their long axes (c axes) parallel in a tubular holder (mass ~5 mg). The geometry of the holder and the crystals thus allowed a rough alignment of the c axis with respect to the field. The magnetization M was measured as a function of field in fields of magnitude 10–40 kOe and was linear at all temperatures outside the range 6–12 K. In this range, $M(H)$ was slightly concave upward, and the low-field susceptibility was inferred by extrapolation.

EPR measurements at 20 GHz on a single crystal over the temperature range 4–300 K show a sharp line whose integrated intensity mirrors the static susceptibility. The g tensor is approximately temperature independent in this range with principal values 2.002, 2.007, and 2.015. The zero of the static susceptibility was obtained from the integrated EPR intensity at 4 K relative to its value at 50 K.

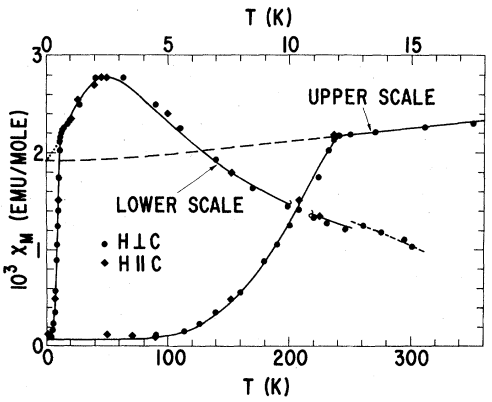

FIG. 2. Magnetic susceptibility of $TTFCuS_4C_4(CF_3)_4$ along two directions. Solid lines are calculated from a spin-Peierls theory, which contains AF chains with uniform exchange above 12 K and temperature-dependent alternating exchange below.

The static susceptibility χ is displayed in Fig. 2. We emphasize that the susceptibility is identical for fields both perpendicular and parallel to the c axis at all temperatures measured. Note that there is a transition at ~250 K. Preliminary x-ray studies in this temperature region show an abrupt decrease of ~3% in the c parameter. While the intrachain interaction is thus enhanced, the basic crystal structure appears to be unchanged.

The susceptibility $\chi(T)$ from 12 to 250 K may be modeled very accurately with a one-dimensional (1-D) AF linear Heisenberg chain of spins ($S=\frac{1}{2}$) and uniform exchange coupling J. Thus the model Hamiltonian is

$$H=\sum_l J(l, l+1)(\vec{S}_l \cdot \vec{S}_{l+1}+\tfrac{1}{4}), \qquad (1)$$

where the sum is over nearest spin neighbors and J is not a function of lattice site l from 12 to 250 K. Using the most reliable calculations[9] of this model currently available, we obtain quite good agreement with the data (Fig. 2) for $g=1.97$ and $J/k_B=77$ K over this range. The uncertainty in J/k_B is about ±2 K. This g value agrees with the EPR g values within experimental error.

From Fig. 2, we see that χ decreases sharply at ~12 K. The usual assumption might be that this behavior signals 3-D AF ordering of the spin system. However, if this were so, χ would decrease to zero for at most one orientation of the sample. Therefore, we must seek a model for which χ decreases to zero in all orientations.

The simplest such model is the 1-D Heisenberg chain with *temperature-independent* alternating exchange. Our calculations using the Bulaevskii[10] formulation of this model and weakly alternating exchange fail to reproduce the sharpness of the decrease of χ at 12 K.

The instability of a 1-D uniform AF chain with respect to spin dimerization has been noted and calculated by several authors in the Ising, X-Y, and Heisenberg models.[3] Pytte[4] has included 3-D lattice dynamics (in the harmonic approximation) and 1-D spin-phonon coupling in the 1-D Heisenberg problem. Using a pseudo-fermion ($\psi_k^\dagger$, ψ_k) representation for the spins, he obtains ($\hbar = k_B = 1$)

$$H = \sum \omega_0(\vec{q}\alpha) b_{\vec{q}\alpha}^\dagger b_{\vec{q}\alpha} + \sum E_k \psi_k^\dagger \psi_k + \sum g(\alpha \vec{q} k)(b_{\vec{q}\alpha} + b_{-\vec{q}\alpha}^\dagger)\psi_k^\dagger \psi_{k-q}, \quad (2)$$

where

$$E_k \equiv pJ\cos(ka),$$

$$g(\alpha\vec{q}k) \equiv 2ig(\alpha\vec{q})p\sin(ka)/[2\omega_0(\vec{q}\alpha)]^{1/2},$$

$$g(\alpha\vec{q}) \equiv \vec{e}(\alpha\vec{q})\cdot\nabla_l J(l, l+1)/(mN)^{1/2},$$

$\vec{e}(\alpha\vec{q})$ is the phonon polarization vector for branch α, and $p(T)$ is the determined self-consistently by

$$p(T) = 1 - 2\sum \frac{\cos(ka)}{\exp(E_k/T)+1}.$$

Equation (2) is just Pytte's Eqs. (10) and (12), except that we have changed to phonon creation and destruction operators ($b_{\vec{q}\alpha}^\dagger$, $b_{\vec{q}\alpha}$). Note that all nonvector momenta are along the chain.

We see that, except for the function $p(T)$, Eq. (2) projected along the chain is essentially a Fröhlich 1-D Hamiltonian. Since we shall be concerned with $T < T_c \ll J$ and p varies very slowly with T in this regime, we may replace $p(T)$ very accurately by $p(0) = 1.637$. We are then free to combine Pytte's results with all mean-field results obtained for a Peierls distortion of the tight-binding Fröhlich Hamiltonian.[11] Thus, the spin-lattice system dimerizes (in zero field) at a temperature T_c given by

$$T_c = 2.28pJ\exp(-1/\lambda), \quad (3)$$

where

$$\lambda \equiv 4g^2p^2/\omega_0^2\pi pJ,$$

$$g \equiv g(\alpha\vec{q}, q = 2k_F),$$

$$\omega_0 \equiv \omega_0(\alpha\vec{q}, q = 2k_F).$$

We have the BCS-like relation

$$2\Delta(0)/T_c = 3.53, \quad (4)$$

where $\Delta(0) = \Delta(T=0)$, and $\Delta(T)$ is the magnetic gap, which follows the usual temperature dependence of the BCS energy gap.

When the lattice dimerizes, two unequal and alternating J's are produced,

$$J_{1,2} = J(1 \pm \delta). \quad (5)$$

Pytte finds

$$\delta = (2g/J)\langle Q\rangle, \quad (6)$$

where

$$\langle Q\rangle \equiv \langle b_{\vec{q}\alpha} + b_{-\vec{q}\alpha}^\dagger\rangle \delta_{q,2k_F}/(2\omega_0)^{1/2}.$$

The angular brackets denote a thermal average over the condensed phonon modes. Established results[11] give

$$\Delta = 2gp\langle Q\rangle \quad (7)$$

and therefore,

$$\delta(T) = \Delta(T)/pJ. \quad (8)$$

Substituting $T_c = 12$ K and $J = 77$ K from the high-temperature data into the above equations, we get

$$\Delta(0) = 21 \text{ K}; \quad \delta(0) = 0.167; \quad \lambda = 0.32. \quad (9)$$

Note that $\delta(T)$ has essentially the same temperature dependence as $\Delta(T)$. Note also that λ, the spin-phonon coupling constant, has a value consistent with the weak-coupling theory of Pytte. As a check on the consistency of setting $p(T) = p(0)$, we calculate $p(12\text{ K}) = 1.626$. This small change in p would, for instance, change the number in Eq. (4) from 3.53 to 3.55.

We now fit the model to the low-temperature data. We calculate the susceptibility of an alternating (dimerized) chain by use of the Bulaevskii[10] model and $J_1(T)/J_2(T)$, given by Eqs. (5), (8), and (9). The Bulaevskii results are scaled to join continuously to the more accurate Bonner-Fisher model where the alternation ceases at $T_c = 12$ K. A small paramagnetic residual, visible in EPR, provides the base line. The curve thus obtained is compared with the data in Fig. 2. The agreement confirms that the theory predicts the magnitude and temperature dependence of J_1/J_2 in the alternating phase.

The theory allows us to predict a BCS-like jump in the magnetic specific heat C_m at T_c. This jump has been calculated for Eq. (2) with a somewhat different fermion dispersion by Kuper,[12] and should have a magnitude of $\sim 0.1R$ ($0.1k_B$ per for-

mula unit). Using Eqs. (2), (6), and (9) and a reasonable value of 90 K[13] for ω_0, the theory predicts a maximum distortion ($T < 4$ K) for the generalized lattice coordinate $\langle Q \rangle$ of ~0.02. This translates roughly to a 0.3% translational distortion along the c axis. Of course, the distortion can be torsional or librational as well as translational. Just above T_c, a soft mode should develop in the phonon spectrum at $(\gamma, \gamma', \pi/c)$ where γ and γ' depend on characteristics of the lattice. As discussed by Pytte, the variation of pseudo-fermion band filling with magnetic field H should have interesting consequences. For instance, his theory predicts a trimerization at $H = 1.1J/g\mu_B \simeq 580$ kOe, under the assumption that nonlinear field effects have not entered.

The good agreement of this mean-field-type theory with experiment may indicate an underlying mean-field character of the transition. In this case, we feel it is probably the 3-D phonon field which is responsible.[14] It would also appear that in other magnetic insulating linear-chain systems, the interchain magnetic coupling dominates the effects of the phonon field, leading to 3-D magnetic rather than spin-Peierls transitions.

We have also examined the isostructural compound $TTFAuS_4C_4(CF_3)_4$ over the temperature range 1.5–300 K. The magnetic behavior is quite similar, with EPR results indicating a spin-Peierls transition at 2.1 K.

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